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(54) Secondary battery.

(57) A secondary battery in which a carbon deposition material made by vapor phase pyrolysis using a hydrocarbon or its derivatives as a raw material is employed as an anode active material and a nonaqueous organic solvent in which a lithium salt is dissolved is employed as an electrolyte. The nonaqueous organic solvent is a mixed solvent of a high dielectric solvent whose donner number is less than 24 and an ethers solvent of a low viscosity whose donner number is less than 24.

Fig .5
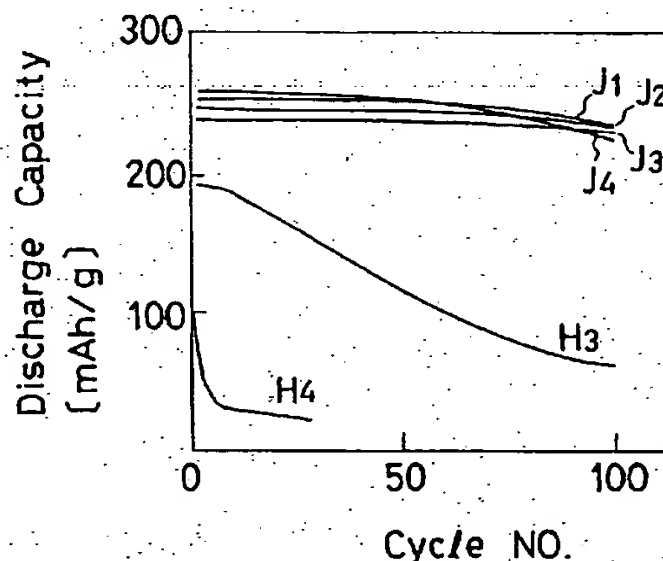
J₁ : PC - THF
J₂ : PC - 2MeTHF
J₃ : EC - THF
J₄ : EC - 2MeTHF
H₃ : DMSO - THF
H₄ : PC - DME

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BACKGROUND OF THE INVENTION

1. Field of the Invention

5   The present invention relates to a secondary battery and, more particularly, to a lithium secondary battery.

2. Description of the Related Art

It has been known that an active carbon material made of hydrocarbon or the like by vapor phase pyrolysis
10 is better than lithium as an anode in a charge and discharge characteristics of a lithium secondary battery. In the battery having the anode formed of the pyrolyzed carbon material, a solution in which a lithium salt such as LiClO$_4$ is dissolved in propylene carbonate (referred to as PC hereinafter) is used as electrolyte because of a high di-electric constant and a wide working range of temperature.

In the case where the carbon material is used as an anode in the lithium secondary battery using a PC
15 solvent, decomposition of PC occurs at charging or discharging. This decomposition can be prevented by employing a carbon deposition material which is obtained by vapor phase pyrolysis using a hydrocarbon or its derivatives at approximately 1000°C (disclosed in Japanese Patent Laying Opened No. 24555/1988 or 311565/1989). However, it is not sufficiently prevented and a battery characteristic is not likely to be further improved.

20 In addition, when the battery is used at a low temperature of 0 to -20°C, anode capacity is reduced, and then battery capacity is also reduced.

In addition, as an organic solvent for dissolving a lithium salt in the lithium secondary battery, there are acetonitrile, propionitrile, propylene carbonate, ethylene carbonate, tetrahydrofuran, dioxane, 1,2-dimethoxy-ethane, nitromethane, N,N-dimethylformamide, dimethyl sulfoxide, sulfolane and butylolactone. In Japanese
25 Patent Laying Opened No. 14881/1989, a mixed solvent made by mixing propylene carbonate and 1,2-dime-thoxyethane in the volume ratio of 1:1 is used.

SUMMARY OF THE INVENTION

30 The present invention was made to solve the above problems. The present invention provides a secondary battery having high capacity and superior in low temperature characteristic and cycle characteristic by selecting an electrolyte suitable for a carbon deposition material obtained by the vapor phase pyrolysis.

According to a secondary battery of the present invention, a carbon deposition material made by vapor phase pyrolysis using a hydrocarbon or its derivatives as a raw material is employed as an anode active material
35 and a nonaqueous organic solvent in which a lithium salt is dissolved is employed as an electrolyte. As the electrolyte, a mixture of a solvent having a high dielectric constant whose donner number is less than 24 and an ether solvent having a low viscosity whose donner number is less than 24 is employed.

Preferably, the above carbon deposition material comprises a skin-core structure in a carbon layer and a carbon material in which an average lattice width of hexagonal graphite ranges 0.3354 to 0.355nm and a peak
40 ratio ranges 0.4 to 1.0 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum. Further preferable carbon deposition material comprises a skin-core structure in 'layer and a mixture of the carbon material in which an average lattice width of hexagonal graphite ranges 0.3354 to 0.3400nm and the carbon material in which an average lattice width ranges 0.343 to 0.355nm. Another preferable carbon deposition material employed in the secondary battery anode material includes a carbon material whose surface layer has a amor-
45 phous,a para-crystal and a turbo strutic structure , in which a lattice width of hexagonal graphite ranges 0.337 to 0.355nm and a peak ratio ranges 0.4 to 1.0 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum.

BRIEF DESCRIPTION OF THE DRAWINGS

50   Fig. 1 is a graph showing the relation between a charge and discharge cycle and discharge capacity at 25°C according to an embodiment 1 of the present invention;
Fig. 2 is a table showing the relation between a charge and discharge cycle and a charge and discharge efficiency at 25°C according to the embodiment 1 of the present invention;
Fig. 3 is a graph showing a charge and discharge characteristic at the first time at 25°C according to the
55   embodiment 1 of the present invention;
Fig. 4 is a graph showing the relation between a charge and discharge cycle and discharge capacity at 0°C according to an embodiment 2 of the present invention;
Fig. 5 is a graph showing the relation between charge and discharge cycle and discharge capacity at 25°C

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according to an embodiment 3 of the present invention;

Fig. 6 is a graph showing the relation between a charge and discharge efficiency at the first time and the donner number at 25°C of respective solvents;

Fig. 7 is a graph for comparing a cycle characteristic of a solvent having a high dielectric constant and an ethers solvent having a low viscosity; and

Fig. 8 is a view showing an apparatus for the pyrolysis of a carbon according to the embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As the above carbon deposition material, preferably its layer has a skin-core structure, in which an average lattice width of hexagonal graphite ranges 0.3354 to 0.355nm and a peak ratio ranges 0.4 to 1.0 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum.

More preferably, the carbon deposition material is a mixture of a carbon material in which a lattice width of hexagonal graphite ranges 0.3354 to 0.3400nm and a carbon material in which a lattice width of that ranges 0.343 to 0.355nm. In evaluating the mixing ratio, a (002) lattice of carbon graphite is measured by using CuKα ray. A diffraction value of the (002) lattice width is represented by a peak ratio of a diffraction value at $2\Theta = 25.0°$ to a maximum diffraction value. In this case, it is preferable that this diffraction ratio ranges 0.03 to 0.90, more preferably ranges 0.03 to 0.50.

In addition, the carbon deposition material is preferably covered with a para-crystal in surface or has a skin-core structure, in which an average lattice width of hexagonal graphite ranges 0.337 to 0.355nm and a peak ratio ranges 0.4 to 1.0 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum.

In addition, the carbon crystal structure in the turbo structic structure has the following characteristics in an X-ray diffraction pattern.

1. A (001) diffraction is broad and its position is shifted to a low angle as compared with pure carbon graphite. Namely, an average lattice width is larger, tailing to the low angle side and showing asymmetrical profile.

2. An (hk) diffraction is rather broad, sharply rising on the low angle side, long tailing to the high angle side and showing asymmetrical profile.

3. An (hkl) diffraction is not recognized.

As the solvent having a high dielectric constant, propylene carbonate, ethylene carbonate, and γ-butyrolactone is appropriate. As the solvent having a low coefficient of viscosity, tetrahydrofuran (THF) or 2 methyl-tetrahydrofuran (2Me THF) is appropriate.

In addition, its mixture ratio of the high dielectric solvent and the low viscosity solvent is preferably 1:4 to 4:1 in volume.

In addition, it is preferable that at least one kind of Li salt such as LiClO$_4$, LiCF$_3$SO$_3$, LiBF$_4$, LiPF$_6$, LiCl+AlCl$_3$, or LiAsF$_6$ is dissolved in the solvent system in 0.5 to 2.0 mol/l. The concentration of Li salt such as LiClO$_4$ in the solvent system is preferably about 1mol/l.

However, the inventors of the present invention have found that even if the carbon material has a similar layer structure, its intercalation characteristic and suitable nonaqueous organic solvents are different, depending on a sight difference on the layer structures. Especially, in a case where the vapor-phase pyrolysis carbon is employed as the anode active material, a nonaqueous organic solvent whose donner number is less than 24 is preferable.

In the secondary battery in which the carbon electrode is employed as the anode active material, Li having an ion radius 0.6Å can be smoothly intercalated into the carbon lattice (a lattice width is 3.354Å to 3.55Å) at charging or can be smoothly deintercalated from the carbon lattice at discharging. However, since a solvent molecule is solvated in Li in an actual electrolyte, it is larger than the ion radius 0.6Å of Li by solvent association. For example, the radius is 3.8Å when PC is solvated and it is 3.4Å or more when DME is solvated (for example, referring to J.Electro-chem. Soc., 128, 2552 (1981)). Therefore, in the battery using intercalation into carbon lattice, it is preferable to employ the solvent which is weakly to be solvated in a solute and which does not prevent intercalation of the solute because the solvent molecule associated with the solute easily dissociates from the surface of the carbon when the solute is intercalated into the carbon lattice. In order to measure the association strength of the solution, there is a donner number proposed by Gutmann. More specifically, the more the donner number is, the more the solution is likely to be associated (referring to Coord. Chem. Rev., 2,239(1967)).

More specifically, by using a solvent of small donner number, the association strength is sufficiently reduced and the solute is not prevented from being intercalated to the vapor-phase pyrolysis carbon material, whereby charge and discharge efficiency can be increased. In addition, in an electrolyte such as DMSO or DME whose donner number is great and which can be likely to be associated in a solute, the solute is intercalated

into the carbon lattice while the solvent molecule is associated (more specifically, an ion molecule larger than the carbon lattice width is intercalated), causing the carbon structure to be destroyed. As a result, the carbon material strips from the electrode and then battery capacity is reduced. However, this does not occur if the solvent whose donner number is less than 24 is employed, and then the capacity is not reduced during a cycling of the charge and the discharge.

In addition, in a case of one solvent, a high dielectric solvent is useful in general speaking. Therefore, the solvent as above is superior to a low viscosity solvent such as ethers. However, an ether of a low viscosity solvent is associated to Li$^+$ more strongly than a high dielectric solvent such as propylene carbonate, ethylene carbonate, γ-butyrolactone and is superior to reduction resistance. Thus, by mixing the both to make electrolyte, decomposition of the high dielectric solvent can be prevented. In addition, viscosity is reduced in the mixed solvent, whereby a preferable electrode characteristic can be provided even at a low temperature.

Besides, any hydrocarbon or derivatives thereof which are conventionally used in the art can be used for the materials for forming the carbon deposition material of this invention.

EXAMPLE

A carbon deposition material was provided by vapor phase pyrolysis using an apparatus shown in Fig. 8. Argon gas was supplied from an argon supply line 1 and propane was supplied from a propane supply line 2. Then, a propane concentration of raw gas was set to 0.13 mole% by handling needle valves 3 and 4. Flow velocity of the raw gas was set to 0.64cm/min and an amount of supply of propane was set to 0.03 mol/h. In a reaction tube 5 was a holder 6 on which an Ni substrate was put and a heating furnace 7 was provided around the reaction tube 5. The holder 6 and the substrate were heated by the furnace 7 at approximately 1000°C for one hour, whereby propane supplied from a Pyrex tube 8 was pyrolytically decomposed and then a pyrolysis carbon film was formed on the Ni substrate. According to the thus obtained carbon material, the lattice width in the C-axis was 0.336nm from a diffraction maximum peak of (002) reflection of graphite in X-ray diffraction using Cu$\kappa\alpha$ ray, a peak ratio was approximately 0.8 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum and a crystallite size Lc in the C-axis direction was approximately 136A. The pyrolytic carbon deposited on the Ni substrate was used as an anode active material as it is and then combined with the following appropriate electrolyte, whereby a lithium secondary battery was made.

Evaluation of the electrolyte appropriate to the anode of this battery was made by using a three-electrode cells in which the anode was a test electrode, Li was a cathode and Li/Li$^+$ was a reference electrode and also by using nonaqueous organic solvent shown in the tables 1 and 2 in which LiClO$_4$ was dissolved in approximate 1 mol/l.

Charge and discharge coulomb efficiency (Fig. 6) and a cycle characteristic of discharge capacity (Fig. 7) were found by performing a charge and discharge cycle test between 0 and 2.5V to Li/Li$^+$ at a constant current of 60mA per 1g of carbon using PC, THF, 2MeTHF, DME, DMSO, τ-BL independently.

As can be seen from Fig. 6, while the charge and discharge coulomb efficiency are considerably lowered in cases of DME and DMSO which are the nonaqueous organic solvent whose donner number is 24 or more, it is improved in cases of PC, THF and 2MeTHF which are the nonaqueous organic solvent whose donner number is less than 24. In addition, as can be seen from Fig. 7, the high dielectric solvent is superior to the low viscosity solvent such as ethers.

EXAMPLE 1

The charge and discharge cycle test was performed between 0 and 2.5V to Li/Li$^+$ at 25°C at a constant current of 60mA per 1g of carbon using PC-THF mixed solvent (volume ratio is 1:1). The discharge capacity at that time was shown by a curve J1 in Fig. 1, the charge and discharge efficiency was shown in Fig. 2 and the charge and discharge curve was shown by a curve J1 in Fig. 3.

In addition, for comparison, the same test was performed in the same condition using PC (shown by a curve H1 in Fig. 1), DMSO-THF mixed solvent (volume ratio 1:1) (shown by a curve H3 in Fig. 3) and PC-DME mixed solvent (volume ratio 1:1) (shown by a curve H4 in Fig. 3).

As a result, it is found that both the efficiency and the cycle characteristic is improved by employing the mixed solvent. In addition, it is found that preferable efficiency and great discharge capacity characteristic can be obtained by using the mixed solvent containing the solvent having a high dielectric constant whose donner number is less than 24 and the ethers solvent having a low coefficient of viscosity whose donner number is less than 24, but, if either of them whose donner number is 24 or more is used, a preferable characteristic is not obtained.

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EXAMPLE 2

The charge and discharge cycle test was performed at a temperature 0°C in the same condition as that of the example 1 using PC-2Me THF mixed solvent (volume ratio 1:1). The discharge capacity at that time was shown by a curve J2 in Fig. 4.

In addition, the same test was performed using PC (shown by a curve H2 in Fig. 4) for comparison.

As a result, it is found that the capacity is increased at a low temperature by employing the mixed solvent.

EXAMPLES 3 AND 4

The charge and discharge test was performed between 0 and 2.5V to Li/Li$^+$ at a constant current of 60mA per 1g of carbon using a mixed solvent of EC-THF (example 3) and EC-2MeTHF (example 4) (volume ratio 1:1). The discharge capacity at that time is shown by curves J3 and J4 in Fig. 5.

In addition, the result in a case of DMSO-THF and PC-DME (shown by curves H3 and H4 in Fig. 4) and the example 1 (J1) and the example 2(J2) are shown together for comparison.

As a result, it is found that the preferable cycle characteristic can be obtained by using the mixed solvent containing the high dielectric solvent whose donner number is less than 24 and the ethers solvent of a low coefficient viscosity whose donner number is less than 24, but, if either of them whose donner number is 24 or more is used, the cycle characteristic is lowered.

Although the above carbon material, preferably its layer has a skin-core structure, in which an average lattice width of hexagonal graphite ranges 0.3354 to 0.355nm and a peak ratio ranges 0.4 to 1.0 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum, the same effect can be expected even using the carbon material which is covered with a para-crystal in surface or has a skin-core structure, in which an average lattice width of hexagonal graphite ranges 0.337 to 0.355nm and a peak ratio ranges 0.4 to 1.0 at a ratio of 1360cm^{-1} to 1580cm^{-1} in argon laser Raman spectrum. This carbon material is covered with a paracrystal in surface or has skin-core structure, in which an active material or irregularities on the carbon surface is preferably in contact with the electrolyte. More preferably, the average lattice width in the para-crystal or the crystal structure of the skin ranges 0.343 to 0.355nm. Further preferably, its core is formed of carbon graphite having an average lattice width ranging 0.3354 to 0.3400nm.

As described above, according to the present invention, there can be provided a secondary battery of high capacity which is superior in charge and discharge efficiency, cycle characteristic and low temperature characteristic, in which an electrolyte suitable for a vapor-phase pyrolysis carbon material can be selected.

While only certain presently preferred embodiments have been described in detail, as will be apparent with those skilled in the art, certain changes and modifications can be made without departing from the scope of the invention as defined by the following claims.

Table 1. Physical and Chemical Properties of High Dielectric Solvents

	Relative Dielectricity [—]	Viscosity [cP]	Melting Point [°C]	Boiling Point [°C]	Density [g·cm⁻³]	Donner Number [—]
Propylene Carbonate (P·C)	64.4	2.53	−49.2	242	1.2	15.1
Ethylene Carbonate (E C)	89.6	1.86	40	248	1.32	16.4
γ-Butyrolactone (γ−BL)	39.1	1.75	−42	206	1.125	---
Dimethyl Sulfoxide (DMSO)	46.5	1.99	18.4	189	1.1	29.8

Table 2. Physical and Chemical Properties of Ether Type Low Viscosity Solvents

	Relative Dielectricity [—]	Viscosity [cP]	Melting Point [°C]	Boiling Point [°C]	Density [g·cm⁻³]	Donner Number [—]
Tetrahydrofuran (THF)	7.25	0.46	−109	66	0.89	20
2·Methyl- Tetrahydrofuran (2Me−THF)	6.24	0.457	----	80	0.85	18
1.2 Dimethoxyethane (DME)	7.2	0.46	−58	85	0.86	24

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Claims

1. A secondary battery comprising as an anode active material a carbon deposition material formed by vapor phase pyrolysis using a hydrocarbon or its derivatives and as an electrolyte a nonaqueous organic solvent in which a lithium salt is dissolved,

   said nonaqueous organic solvent being a mixed solvent of a high dielectric solvent whose donner number is less than 24 and an ether solvent of a low viscosity whose donner number is less than 24.

2. A secondary battery according to claim 1, wherein said carbon deposition material comprises a carbon material in which an average (002) lattice width of hexagonal graphite at C axis ranges 0.3354 to 0.355nm by using CuKα ray and a peak ratio ranges 0.4 to 1.0 at a ratio of $1360cm^{-1}$ to $1580cm^{-1}$ in argon laser Raman spectrum.

3. A secondary battery according to claim 2, wherein said carbon deposition material comprises a mixture of a carbon material in which an average lattice width of hexagonal graphite ranges 0.3354 to 0.3400nm, and a carbon material in which an average lattice width ranges 0.343 to 0.355nm.

4. A secondary battery according to claim 1, wherein said carbon deposition material comprises a carbon material which is covered with an amorphous structure, a para-crystal or a turbo strutic structure in surface.

5. A secondary battery according to claim 1, wherein said carbon deposition material is covered with the turbo strutic structure, in which a lattice width of hexagonal graphite ranges 0.337 to 0.355nm and a peak ratio ranges 0.4 to 1.0 at a ratio of $1360cm^{-1}$ to $1580cm^{-1}$ in argon laser Raman spectrum.

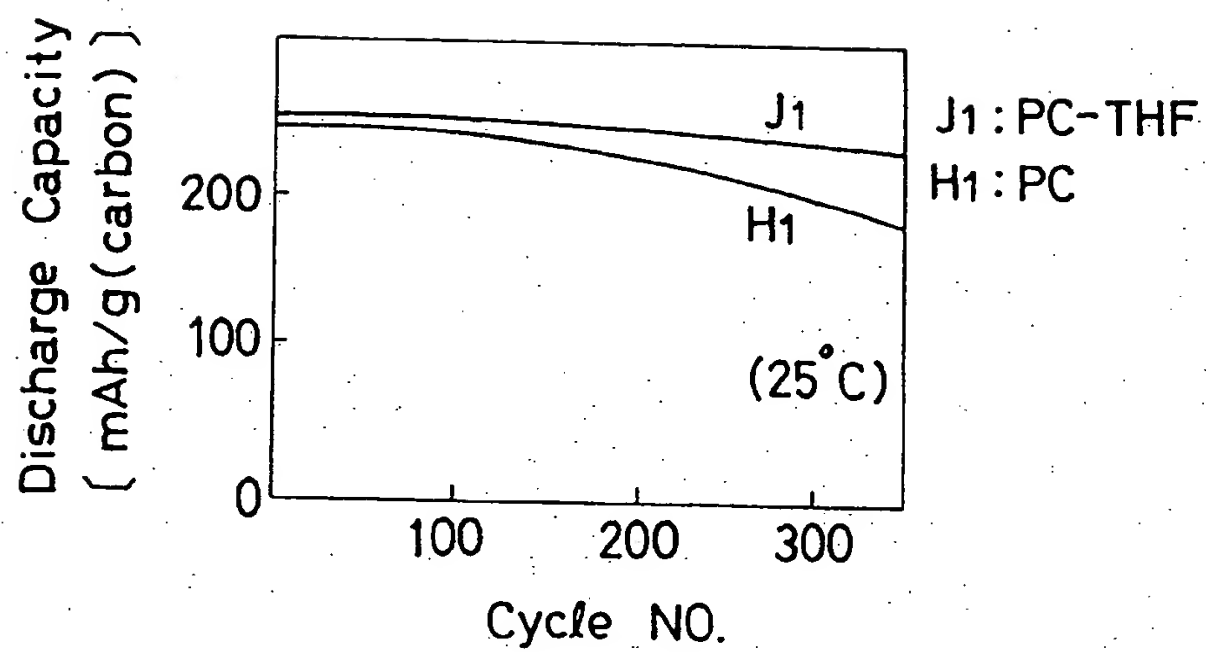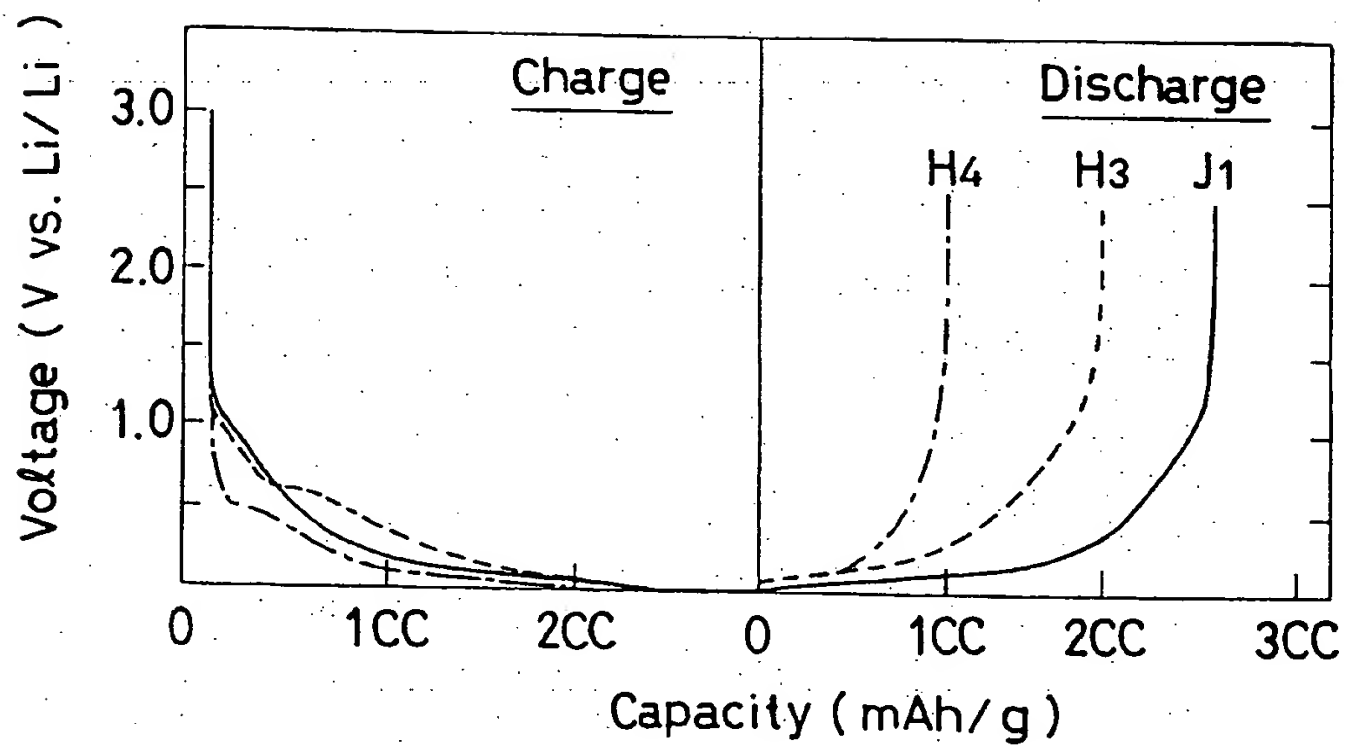6. A secondary battery according to claim 1, which is adapted to a lithium secondary battery.

Fig.1

Fig.2

Cycle NO.	Charge/ Discharge Efficiency [%]	
	PC-THF Electrolyte	PC Electrolyte
1	90	86
10	98	96
50	97	95

Fig.3

J1 : PC-THF
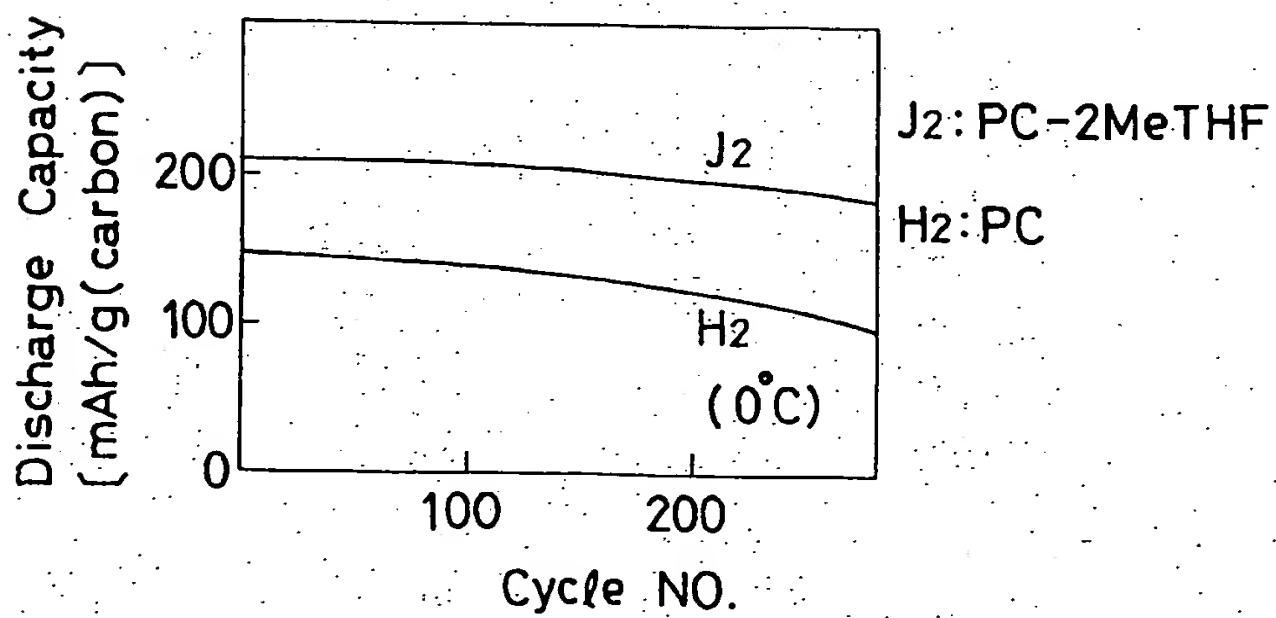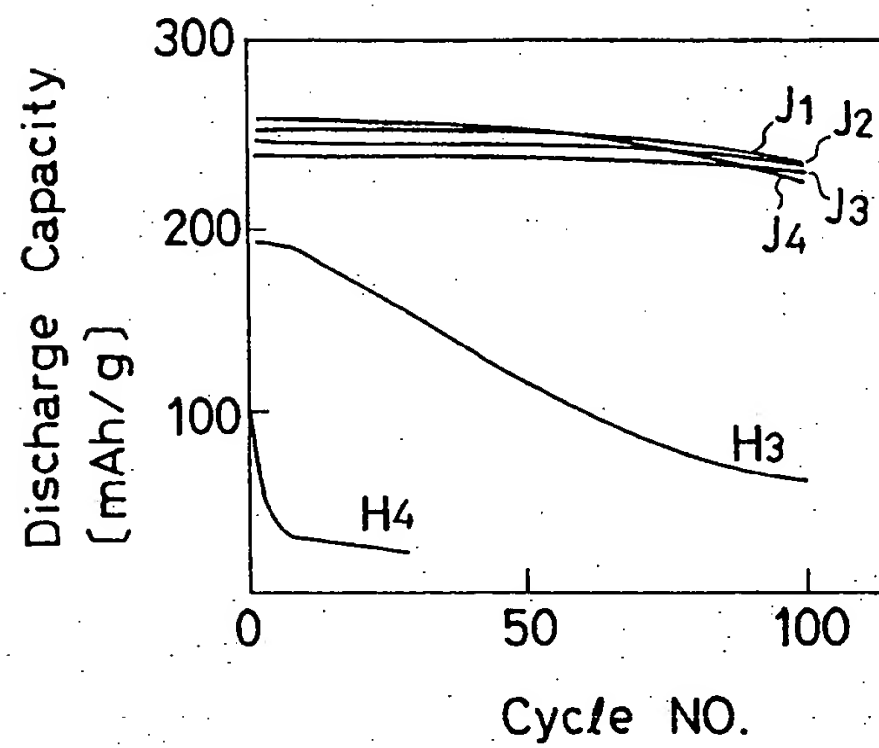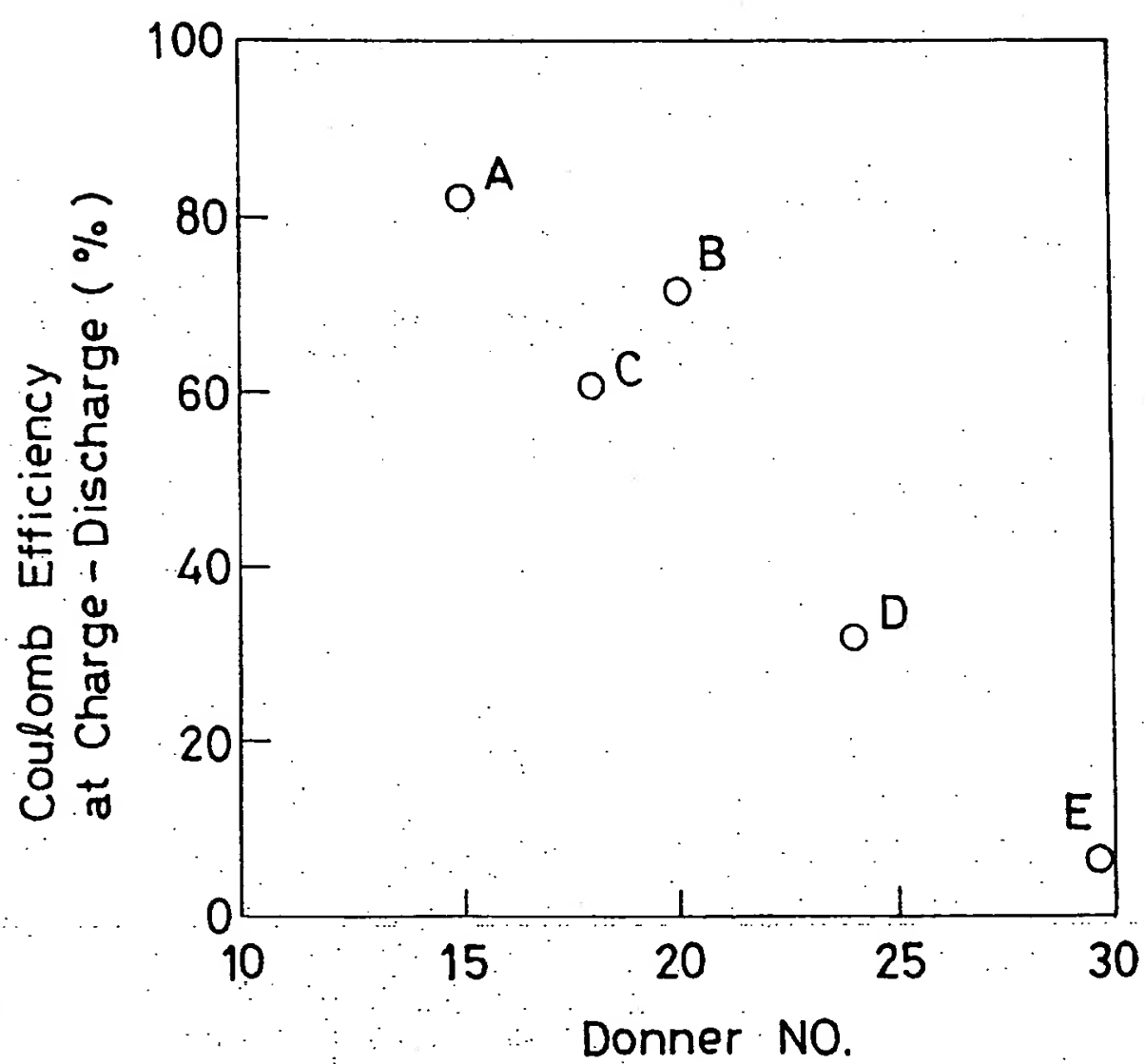H3 : DMSO-THF
H4 : PC-DME

Fig.4

J2 : PC-2MeTHF
H2 : PC

Fig .5

J₁ : PC-THF
J₂ : PC-2MeTHF
J₃ : EC-THF
J₄ : EC-2MeTHF
H₃ : DMSO-THF
H₄ : PC-DME

Fig .6
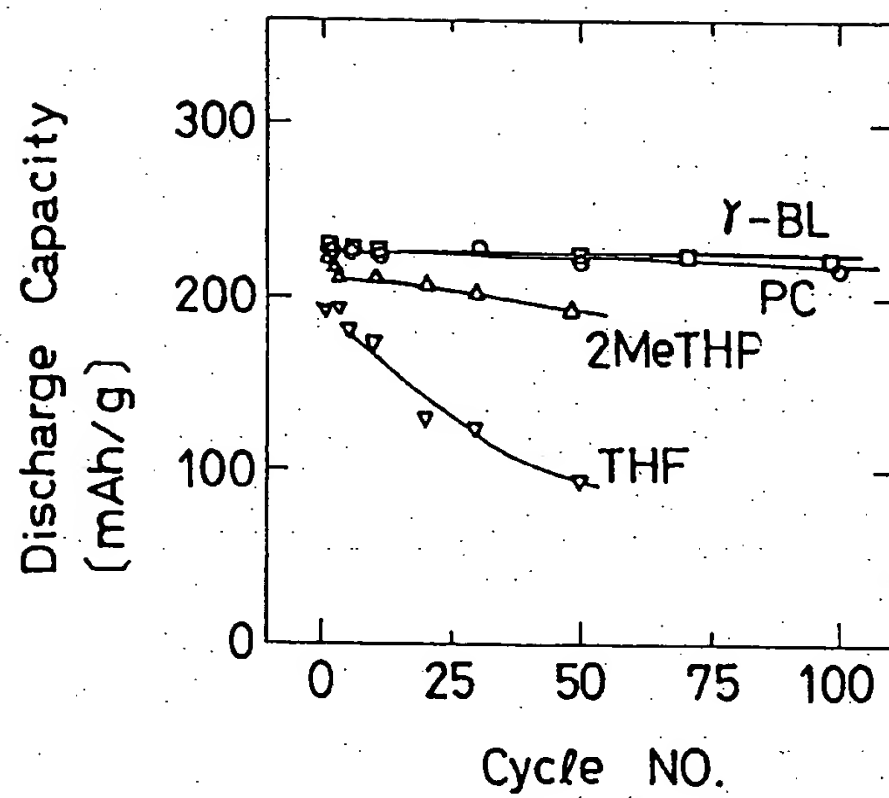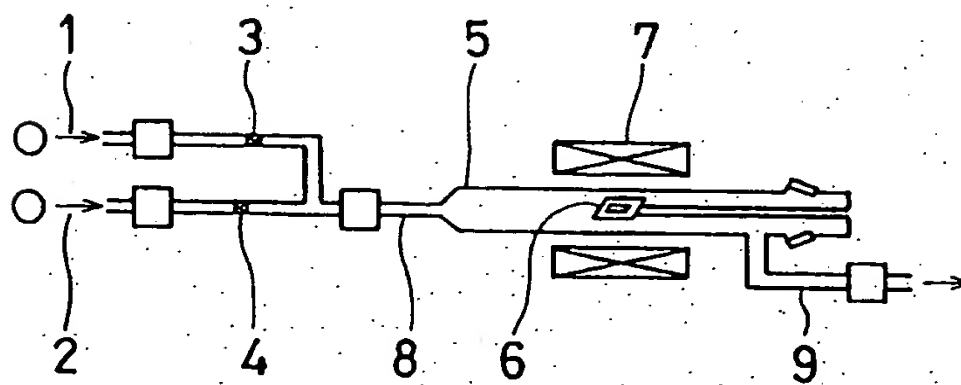

A : PC
B : THF
C : 2MeTHF
D : DME
E : DMSO

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Fig.7

Fig.8

European Patent
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EUROPEAN SEARCH REPORT

Application Number

	DOCUMENTS CONSIDERED TO BE RELEVANT		EP 92302936.7
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP - A - 0 434 402 (SHARP) * Claim 1; page 4, lines 33-36 * --	1,6	H 01 M 10/40 H 01 M 4/58 H 01 M 4/40
A	EP - A - 0 404 578 (SHARP) * Abstract * --	1,6	
A	CHEMICAL ABSTRACTS, vol. 110, no. 10, March 6, 1989, Columbus, Ohio, USA YOSHIO M. et al. "The importance of the donor and acceptor concept in tailoring nonaqueous mixed electrolytes for lithium secondary batteries" page 229, column 1, abstract-no. 79 271k & Prog. Batteries Sol. Cells 1988, 7, 377-9 --	1,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D,A	CHEMICAL ABSTRACTS, vol. 110, no. 20, May 15, 1989, Columbus, Ohio, USA TAKAHASHI YUZURU et al. "Secondary batteries with lithium-carbon anodes" page 216, column 1, abstract-no. 176 729y & Jpn. Kokai Tokkyo Koho JP 01 14,881 --	1,6	H 01 M
D,A	EP - A - 0 239 410 (SHARP) * Examples * ----	1,6	

The present search report has been drawn up for all claims		
Place of search VIENNA	Date of completion of the search 13-07-1992	Examiner LUX

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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